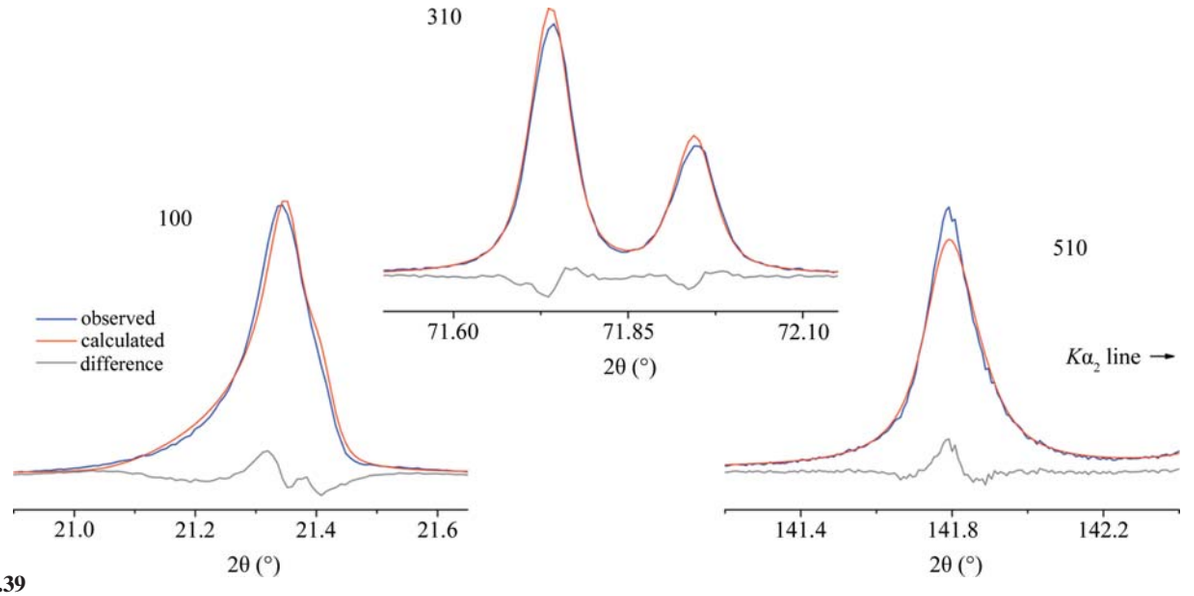


**Figure 3.1.39**
Fits of three SRM 660b lines obtained with a Rietveld analysis using the Thompson, Cox and Hastings formalism of the pseudo-Voigt PSF and the Finger model for asymmetry. *TOPAS* was used for the analysis.

quent analyses of unknowns. This approach tends to result in stable and robust refinements. Parameters can, therefore, be considered as falling into three groups: those that are specific to any given sample and are always refined, ones that are specific to the IPF and are refined using only high-quality data from standards, and lastly the highly determined parameters that are refined only as a basic test of the model.

To consider the Thompson, Cox & Hastings (1987) (TCH) formalism of the pseudo-Voigt PSF with the Finger model for asymmetry, which is common to many Rietveld codes, a Rietveld analysis of SRM 660b was performed using *GSAS* (using the type-3 PSF) and *TOPAS* (using the PV_TCHZ peak type). The TCH formalism allows for the direct refinement of the Gaussian and Lorentzian FWHM values. The Caglioti function was used; Lorentzian terms were constrained as per equation (3.1.2). The *S*/*L* and *H*/*L* terms are highly correlated; *S*/*L* was refined, while *H*/*L* was adjusted manually so that the two terms were nearly equal. Additional parameters that were refined included the lattice parameters, sample displacement and transparency terms, Chebyshev polynomial terms (typically 5 to 7) to represent the background, scale factors, the type-0 Lorentz–polarization term (*GSAS*), the Cu $K\alpha_1/K\alpha_2$ ratio, and structural parameters. With this strategy, the sample shift and transparency aberration functions, in conjunction with the Finger asymmetry model, were used to model the data of Fig. 3.1.26. Given that the Finger model is not entirely appropriate for divergent-beam laboratory data, the sample shift and transparency terms may refine to non-physical values. They will, however, correctly indicate relative values for sample *z* height and transparency. The model for specimen transparency in *TOPAS* is the asymmetric function illustrated in Fig. 3.1.10, while the model in *GSAS* consists of a profile displacement in $\sin 2\theta$. The TCH/Finger formalism of *TOPAS* reproduced the certified lattice parameter and resulted in a GoF of 1.5, whereas the GoF value realized with *GSAS* was 1.85. Fig. 3.1.39 displays the fit quality of the 100, 310 and 510 reflections obtained with *TOPAS*. The fit to the asymmetry of the 100 reflection is reasonable, with a 0.007° shift in position. The fit to the 510 reflection is not dissimilar to that shown in Fig. 3.1.32, indicating that the Caglioti function is working analogously to the manner previously discussed. The improvement in fit with the *TOPAS* implementation was most notable around the 70 to 90° $2\theta$ region, where the transparency effects are at a maximum. These results validate the TCH/Finger formalism and constitute a valid calibration for this equipment and data-analysis method; the utility of the aberration function for specimen transparency as documented by Cheary & Coelho (1992) is demonstrated.

Differentiating between the profile-shape terms that are specific to the IPF and those refined to consider the microstructure of unknowns yields a stable refinement strategy when using the TCH/Finger formalism. The profile parameters *GU*, *GV*, *GW*, *LX*, *LY*, *S*/*L* and *H*/*L* as determined from SRM 660b constitute the IPF and are fixed, or used as floors, in subsequent refinements (Cline, 2000). The IPF for the NIST machine was described with only the *GW*, *LX* and *LY* parameters. In subsequent analyses only the *GP*, *GU*, *LX* and *LY* terms were refined to represent Gaussian size and microstrain and Lorentzian size and microstrain broadening, respectively, and thus yield microstructural information from the sample. Parameters that tend to values less than the IPF were fixed at IPF values. The Finger asymmetry parameters determined from the standard need not be refined with unknowns; it has, however, been observed that doing so will neither substantially improve the quality of the fit, nor will it result in instability. Additional parameters that are always refined with unknowns include: scale factors, lattice parameters, specimen displacement and transparency terms, background terms, and structural parameters.

While an analysis of SRM 660*x* permits the calibration of the instrument with respect to profile shape and position, it is also desirable to evaluate parameters related to the diffraction intensity. However, the analysis of data from high-symmetry materials such as silicon and lanthanum hexaboride may result in some degree of instability with the refinement of the intensity-specific parameters, perhaps because of the relatively small number of lines. Use of SRM 676a addresses this difficulty (Fig. 3.1.40). With this analysis, the Lorentz–polarization factor refined to a credible value and structure parameters were within the bounds of those obtained from the high-*q*-range experiments performed in the certification of SRM 676a (Cline *et al.*, 2011).

We start the discussion on the FPA method for instrument calibration by listing the parameters specific to the IPF that